

- Chem.* 1996, 35, accepted.
9. Brown, I. D.; Altermatt, D. *Acta Crystallogr.* 1985, B41, 244.
10. Hatfield, W. E. *J. Appl. Phys.* 1981, 52, 1985.
11. Harrison, W. T. A.; Vaughey, J. T.; Jacobson, A. J.; Goshorn, J. W. *J. Solid State Chem.* 1995, 116, 77.
12. Whangbo, M. H. private communication.
13. Banerjee, D. *Coordination Chemistry*; McGraw-Hill: Delhi, 1993, p 212.

## Dioxygen Binding to the Singly Alkoxo-Bridged Diferrous Complex: Properties of $[\text{Fe}^{\text{II}}_2(\text{N-Et-HPTB})\text{Cl}_2]\text{BPh}_4$

Eunsuk Kim<sup>†</sup>, Kang-Bong Lee<sup>‡</sup>, and Ho G. Jang<sup>†\*</sup>

Contribution from the <sup>†</sup>Department of Chemistry, Korea University, Seoul 136-701, Korea

<sup>‡</sup>Advanced Analysis Center, KIST, Seoul 136-130, Korea

Received August 1, 1996

$[\text{Fe}^{\text{II}}_2(\text{N-Et-HPTB})\text{Cl}_2]\text{BPh}_4$  (**1**), where N-Et-HPTB is the anion of *N,N,N',N'*-tetrakis(*N*-ethyl-2-benzimidazolylmethyl)-2-hydroxy-1,3-diaminopropane, has been synthesized to model dioxygen binding to the diferrous centers of proteins. **1** has a singly bridged structure with a  $\mu$ -alkoxo of N-Et-HPTB and contains two five-coordinate iron(II) centers with two chloride ligands as exogenous ligands. **1** exhibits an electronic spectrum with a  $\lambda_{\text{max}}$  at 336 nm in acetone. **1** in acetone exhibits no EPR signal at 4 K, indicating diiron(II) centers are antiferromagnetically coupled. Exposure of acetone solution of **1** to  $\text{O}_2$  at  $-90^\circ\text{C}$  affords an intense blue color intermediate showing a broad band at 586 nm. This absorption maximum of the dioxygen adduct(**1**/ $\text{O}_2$ ) was found in the same region of  $\mu$ -1,2-peroxo diiron(III) intermediates in the related complexes with pendant pyridine or benzimidazole ligand systems. However, this blue intermediate exhibits EPR signals at  $g = 1.93, 1.76$ , and  $1.59$  at 4 K. These  $g$  values are characteristic of  $S = 1/2$  system derived from an antiferromagnetically coupled high-spin  $\text{Fe}(\text{II})\text{Fe}(\text{III})$  units. **1** is the unique example of a ( $\mu$ -alkoxo)diferrous complex which can bind dioxygen and form a metastable mixed-valence intermediate. At ambient temperature, most of **1**/ $\text{O}_2$  intermediate decays to form a diamagnetic species. It suggests that the decay reaction of the intermediate might be bimolecular, implying the formation of mixed-valence tetranuclear species in transition state.

### Introduction

Dioxygen binding of the diferrous compounds has been of interest in recent years because of its relevance to iron-oxo proteins.<sup>1</sup> For example, diferrous sites of the reduced forms of hemerythrin (Hr),<sup>2,3</sup> ribonucleotide reductase (RNR),<sup>4,5</sup> and methane monooxygenase (MMO)<sup>6,7</sup> have been shown or postulated to interact with dioxygen and to be responsible for oxygen activation. DeoxyHr reversibly binds dioxygen to form oxyHr, characterized as a ( $\mu$ -oxo)( $\mu$ -carboxylato)diiron(III) complex with a terminally bound hydroperoxide.<sup>3,8</sup> On the other hand, dioxygen reacts with reduced RNR and MMO irreversibly to afford oxidizing species capable of generating a catalytically essential tyrosyl radical and hydroxylating alkanes, respectively.<sup>4-7</sup>

A variety of diiron(III) complexes has been reported as structural and spectroscopic models for the inactive forms of the non-heme diiron proteins.<sup>1,9</sup> However, only a limited number of diiron(II) complexes have been reported as models for non-heme enzymes.<sup>10-13</sup> The chemistry of diiron(II) complexes are of importance to gain insight into the structures and functions of the active forms of the above metalloproteins, especially with respect to the binding mode and activation of dioxygen, and the oxygenation mechanism.

Although there are several  $\mu$ -peroxo diiron complexes generated by the reaction of iron(III) complexes with hydrogen peroxide,<sup>14</sup> only a few iron(II) complexes which can bind  $\text{O}_2$  in a  $\mu$ -peroxo form have been known. For instance, complexes with ( $\mu$ -alkoxo or hydroxo)( $\mu$ -carboxylato)diferrous cores such as  $[\text{Fe}^{\text{II}}_2\{\text{HB}(3,5\text{-i-Pr}_2\text{pz})_3\}_2(\text{OH})(\text{OBz})]$ ,<sup>15,16</sup>  $[\text{Fe}^{\text{II}}_2(\text{N-Et-HPTB})(\text{OBz})](\text{BF}_4)_2$ ,<sup>17</sup> and  $[\text{Fe}^{\text{II}}_2(\text{HPTP})(\text{OBz})](\text{BF}_4)_2$ <sup>17b</sup> bind  $\text{O}_2$  to form ( $\mu$ -1,2-peroxo)diiron(III) adducts. These complexes all have five-coordinate iron(II) centers with vacant sites for ligand binding, but  $\text{O}_2$  binding is irreversible. By introducing methyl groups at the 6-positions of the pendant pyridines of HPTP, Hayashi *et al.* obtain  $[\text{Fe}^{\text{II}}_2(\text{Me}_6\text{-TPDP})(\text{OBz})(\text{H}_2\text{O})](\text{BF}_4)_2$  which binds  $\text{O}_2$  reversibly.<sup>18</sup>

In this paper, we report the properties of  $[\text{Fe}^{\text{II}}_2(\text{N-Et-HPTB})\text{Cl}_2]\text{BPh}_4$  (**1**) which has a ( $\mu$ -alkoxo)diiron(II) core unsupported by other bridges; this complex also binds dioxygen. We investigated the  $\text{O}_2$  binding ability and activation process of diferrous complex by changing the Lewis acidity of the iron center *via* changing the ligand environment.

### Experimental Section

**Synthesis.** The dinucleating ligand H-N-Et-HPTB was synthesized using the published procedures.<sup>19</sup> 1,2-Diaminobe-

nzene (10.55 g, 0.097 mol) was ground to a fine powder and mixed with 2-hydroxy-1,3-diaminopropanetetraacetic acid (5.0 g, 0.016 mol). The mixture was heated at 170–180 °C for 1 hour at which stage effervescence had ceased. After the mixture was cooled, the resulting red glass was taken up in dilute (~4 M) hydrochloric acid (~150 mL), and a grayish blue precipitate was slowly formed. After the solution was filtered, this precipitate was washed by slurring in acetone several times. The precipitate was then dissolved in water and neutralized with dilute ammonia. The white precipitate was collected, recrystallized from acetone, and ground to a fine powder prior to vacuum drying (yield, ~90%). After dried, this material was suspended in dry THF and stirred overnight with NaOH (1.4 g). Bromoethane (9 g) was added, and the solution was left stirring for 2 days. The solvents were stripped to dryness and the resulting powder dissolved in chloroform. The insoluble NaBr was removed by filtration, and the filtrate was stripped to a very small volume. A little acetone was added and upon standing a white powder was obtained (yield, 80%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm): 1.1 (t, 12H), 2.7 (d, 4H), 3.95 (q, 8H), 4.0 (s, 8H), 7.4 (m, 16H). Mass spectrometry (positive ion FAB):  $m/z$ , 723.

$[\text{Fe}^{II}_2(\text{N-Et-HPTB})\text{Cl}_2]\text{BPh}_4$  (**1**) was prepared under argon by dissolving H-N-Et-HPTB (0.36 g, 0.5 mmol) and  $\text{Et}_3\text{N}$  (0.07 mL, 1.0 mmol) in 10 mL methanol and transferring the solution anaerobically to the methanolic solution of  $\text{FeCl}_2$  (0.254 g, 1.0 mmol). The addition of a degassed methanol solution of  $\text{NaBPh}_4$  (0.171 g, 0.50 mmol) yielded an ivory precipitate, which was filtered, dried *in vacuo* and recrystallized from acetonitrile/ether.

Dioxygen adduct of **1** was prepared by chilling the anaerobic precursor solution of **1** to –90 °C and exposed to  $\text{O}_2$ .

**Physical Measurements.**  $^1\text{H}$  NMR spectra were obtained on Varian Unity plus 300 and Unity plus 600 spectrometers. The paramagnetic  $^1\text{H}$  NMR spectra were obtained using a 90° pulse with 16 K data points. An inversion-recovery pulse sequence (180°- $\tau$ -90°-AQ) was used to obtain non-selective proton relaxation times ( $T_1$ ).

A typical magnitude  $^1\text{H}$ -COSY spectrum was collected with 1024 data points in  $t_2$  and 256 data points in  $t_1$  with a band width of 10 kHz and a repetition time of <0.2 s. The time for the data collection for a ~10 mM sample was about 8 hrs. A zero-degree shifted sine bell was applied in both dimensions and zero-filled to 2048  $t_2 \times 2048$   $t_1$  data points prior to Fourier transformation and symmetrization. In this study, cross signals from pairs of signals with  $\Delta\delta < 1$  ppm in a spectral width of ~30 ppm could be clearly recognized under proper processing procedures.

Electronic spectra were measured on an HP 8452A diode array spectrometer. Low temperature visible spectra were obtained using an immersion dewar equipped with quartz windows (H.S. Martin Inc. Visible-UV Dewar/cell). FAB Mass spectrum was performed on VG70-VSEQ (VG Analytical, UK). X-band EPR measurements were performed with Bruker ESP-300S spectrometer equipped with an Oxford liquid helium cryostat.

## Results and Discussion

### Properties of the Diron(II) Precursor. $[\text{Fe}^{II}_2(\text{N-Et-}$

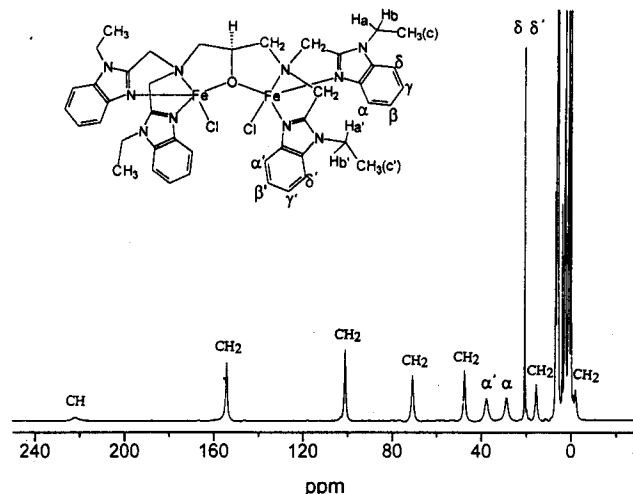


Figure 1.  $^1\text{H}$  NMR spectrum of **1** in  $\text{CD}_3\text{CN}$ .

$\text{HPTB})\text{Cl}_2]\text{BPh}_4$  (**1**) is extremely air-sensitive ivory solid, the color of which arises from UV absorption band. **1** exhibits an intense band in acetone at 336 nm ( $\epsilon \approx 2.0 \times 10^3$ ) which is similar value of the related complexes with pendant pyridine or benzimidazole ligand systems.<sup>17,18</sup> The lack of low energy visible absorption bands despite the presence of nitrogen ligands suggests that this is a high-spin iron(II) complex. Unlike deoxyHrN<sub>3</sub><sup>20</sup> and reduced MMO,<sup>21</sup> the frozen solution of **1** at 4 K exhibits no EPR signal which is characteristic of an antiferromagnetically coupled diferrous centers.<sup>17</sup>

The NMR spectrum of **1** displays relatively sharp well-resolved resonances due to the very favorable electronic relaxation time of the ferrous centers (Figure 1).<sup>22,23</sup> The peaks were spread over a 200 ppm range. Most of protons can be assigned by comparison of integration,  $T_1$  values (Table 1) and COSY connectivities (Figure 2); the COSY information was particularly useful for identifying the ring protons of pendant benzimidazole ligands.

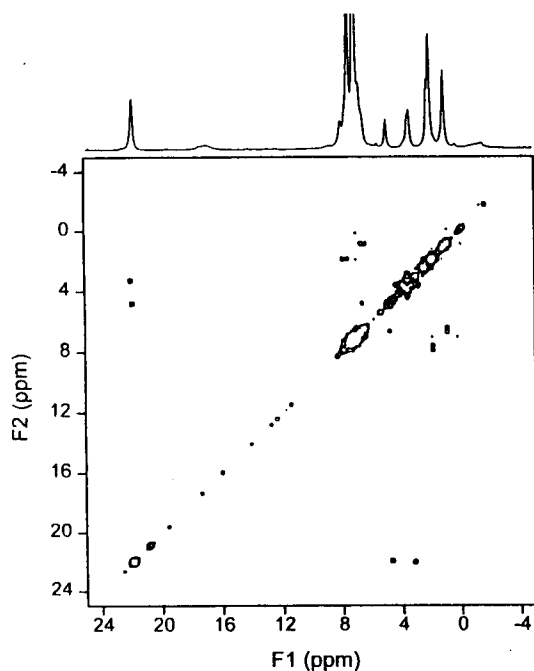
All the  $\text{CH}_2$  and CH protons were observed. The sole methine proton, being geminal to the bridging alkoxide, was readily assignable by its single-proton integration and large shift due to its proximity to the iron(II) centers. However, it was too broad to measure the  $T_1$  value. The methylene protons appear as six resonances with very short  $T_1$  values and two-proton integrations each; the number of resonances observed suggests that there is a two-fold axis symmetry relating the two halves of the molecule. Thus, the six  $\text{CH}_2$  resonances would arise in the half-molecule from the two protons on the hydroxypropane backbone and the four protons associated with the benzimidazole arms. Their individual isotropic shifts reflect the orientation of the C-H bonds in the chelate rings which modulates the amount of spin delocalization.<sup>23</sup>

The COSY spectrum of **1** (Figure 2) shows a number of cross peaks and identifies the various multi-spin systems present in the complex. For instance, the protons of the N-ethyl group form an  $\text{ABX}_3$  spin system, while the  $\beta$ ,  $\gamma$ , and  $\delta$  protons of the benzimidazole constitute an AMX unit. However,  $\alpha$  protons of the benzimidazole being too close to the metal centers have  $T_1$  values too short to permit its connectivity to the corresponding  $\beta$  protons to be observed;

**Table 1.** NMR parameters and the Relaxation Times of **1**

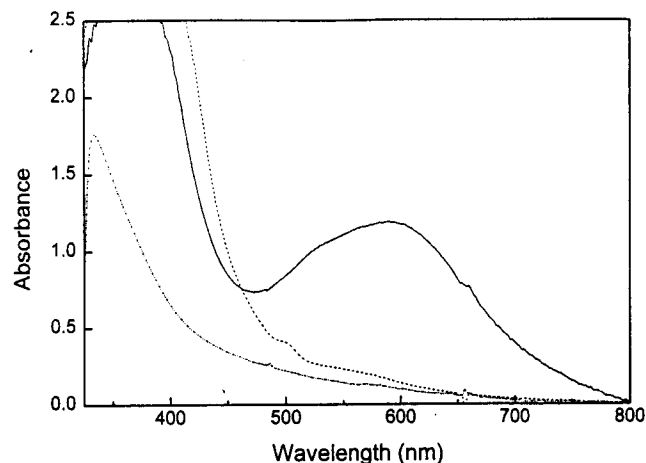
Peak	Chemical shift (ppm)	T <sub>1</sub> (ms)
CH	~222	nd
CH <sub>2</sub>	153.0	2.1
CH <sub>2</sub>	100.9	2.2
CH <sub>2</sub>	71.1	2.4
CH <sub>2</sub>	48.0	1.4
CH <sub>2</sub>	16.3	1.3
CH <sub>2</sub>	-0.9	1.6
α	29.6	1.3
β	6.8	27
γ	4.9	46
δ	21.5	33
a	~6.4	nd
b	~6.9	nd
c	1.0	28
α'	38.0	0.7
β'	3.8	17
γ'	3.4	50
δ'	21.6	34
a'	8.1	16
b'	7.9	16
c'	2.3	37

Greek letters designate positions of benzimidazole rings; a, b, and c designate the diastereopic CH<sub>2</sub> and CH<sub>3</sub> protons of the *N*-ethyl groups of *N*-Et-HPTB, respectively.

**Figure 2.** COSY spectrum of **1** in CD<sub>3</sub>CN.

we assign them to remaining unassigned features with appropriately T<sub>1</sub> values.

Several factors contribute to these core features. Most important is the absence of supporting bridges. Iron centers are bridged only through the alkoxo bridge. Furthermore,

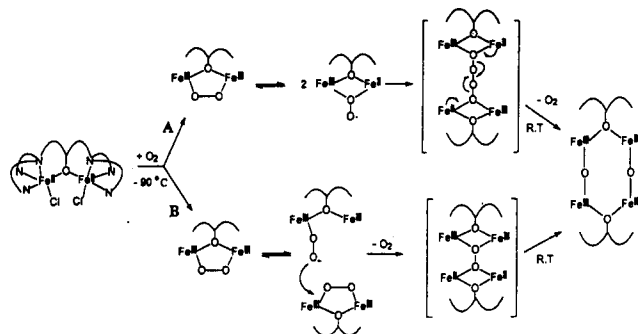
**Figure 3.** UV/visible spectra of **1** (dashed line), **1**/O<sub>2</sub> adduct (solid line), and the decomposed **1**/O<sub>2</sub> adduct (dotted line) in acetone at -85 °C.

each iron center has a five-coordination geometry with chloride ion as exogenous ligand.

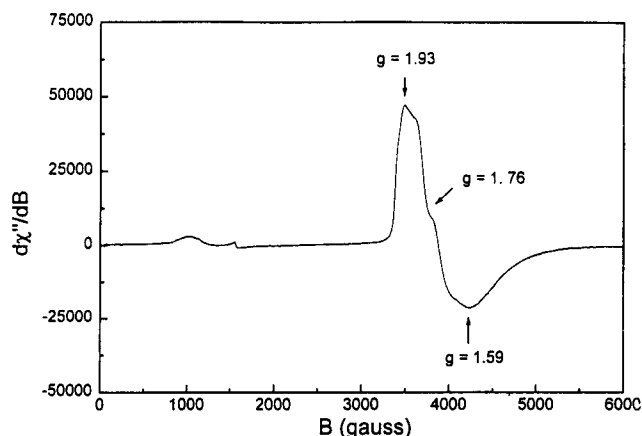
**Spectroscopic characterization of the dioxygen adduct.** The diferrous complex **1** reacts with O<sub>2</sub> and the resulting intermediate can be stabilized at low temperature to allow its spectroscopic characterization. Exposure of the acetone solution of **1** to O<sub>2</sub> at -90 °C affords a species with an intense blue color corresponding to a visible band at near 586 nm (Figure 3). However, application of a vacuum does not change the color of the dioxygen adduct, indicating an irreversible adduct formation. When compared to those of other diferric peroxide complexes, the absorption maximum of the **1**/O<sub>2</sub> adduct near 586 nm is similar to those of dioxygen adducts of [Fe<sup>II</sup><sub>2</sub>(*N*-Et-HPTB)(OBz)](BF<sub>4</sub>)<sub>2</sub> (588 nm),<sup>17</sup> [Fe<sup>II</sup><sub>2</sub>(HPTP)(OBz)](BF<sub>4</sub>)<sub>2</sub> (562 nm),<sup>17b</sup> and [Fe<sup>II</sup><sub>2</sub>(Me<sub>4</sub>-TPDP)(OBz)(H<sub>2</sub>O)](BF<sub>4</sub>)<sub>2</sub> (616 nm).<sup>18</sup> These absorption bands arise from the peroxo-to-Fe(III) charge transfer transitions which were confirmed by resonance Raman studies. Thus, the absorption band of **1**/O<sub>2</sub> might arise from the peroxo-to-Fe(III) charge transfer transition. Dioxygen presumably binds to the open coordination sites of the diferrous complex and is reduced to the peroxo state by the iron centers.

Interestingly, **1**/O<sub>2</sub> displays strong EPR signals at *g* = 1.93, 1.76, and 1.59 (rhombic symmetry) and weak signals at *g* = 7.0 and 4.3 (high-spin iron(III) impurity). These strong signals (*g* < 2.0) are characteristic of antiferromagnetic coupling between a high-spin Fe<sup>III</sup> (*S* = 5/2) and a high-spin Fe<sup>II</sup> (*S* = 2) ions, resulting in an *S*<sub>total</sub> = 1/2 ground state.<sup>24</sup> It is a unique alkoxo bridged diiron complex having a mixed-valence intermediate. There are two possible forms of this mixed-valence intermediate; one is Fe<sup>II</sup>Fe<sup>III</sup>-superoxo radical species in pathway A, the other is a (μ-peroxo)Fe<sup>II</sup><sub>2</sub>Fe<sup>III</sup><sub>2</sub> species in pathway B (Scheme 1).<sup>25</sup> Even though it is not determined yet, the latter form might be more favorable since it does not show any EPR signal corresponding to organic radical species.

The spectral properties of the **1**/O<sub>2</sub> intermediate were not changed at -90 °C for several hours. However, they were changed significantly upon warming the intermediate to room temperature. It showed no visible absorption band and a



**Scheme 1.** Proposed decay mechanism of  $1/\text{O}_2$  adduct.

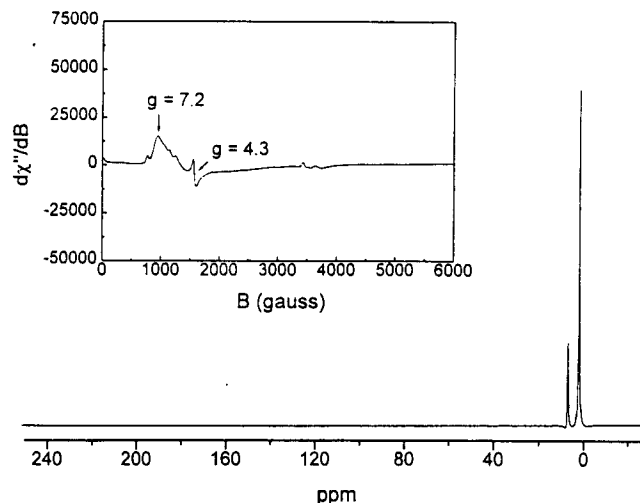


**Figure 4.** EPR spectrum of a frozen solution of  $1/\text{O}_2$  adduct in acetone at 4 K. Instrumental parameters: microwave frequency, 9.42 GHz; power, 5 mW; modulation frequency, 100 kHz; modulation amplitude, 5.08; gain,  $2.5 \times 10^4$ .

diamagnetic NMR spectrum pattern. However, it exhibits weak EPR signals at  $g = 7.2$  and  $4.3$  corresponding to the small amount of monomeric high-spin  $\text{Fe(III)}$  species (Figure 5). Thus, the  $1/\text{O}_2$  intermediate would appear to have decomposed upon warming to the  $(\mu\text{-oxo})\text{polyiron(III)}$  complex (Scheme 1). Similarly, in a previous X-ray study of diiron(III) complex,  $[\text{Fe}_2(\text{HPTB})(\text{OBz})_2](\text{ClO}_4)_3$ , revealed aggregation of two dinuclear units to form a tetranuclear species,  $[\text{Fe}_4\text{O}_2(\text{HPTB})_2(\text{OBz})_2]^{4+}$ .<sup>26</sup>

Complex **1** expands the list of diferrous complexes which can bind dioxygen. But it is very unique model since it is the only complex with a single alkoxo bridged diiron(II) centers.  $\text{O}_2$  probably binds to the iron centers as peroxo species and convert to dimeric mixed-valence complexes. The increasing availability of these complexes with related structures enhances the prospects of elucidating the principles of dioxygen binding to those novel centers.

**Concluding Remarks.** New diiron(II) complex with only alkoxide bridge,  $[\text{Fe}^{\text{II}}_2(\text{N-Et-HPTB})\text{Cl}_2]\text{BPh}_4$ , was synthesized and characterized. We can control the thermal stability of  $\mu\text{-peroxo}$  diiron(III) complex by substituting a benzoate ligand with two anionic chloride ligands. Consequently, the Lewis acidity of the metal center was decreased and gives rise to lower temperature ( $-90^\circ\text{C}$ ) for  $\text{O}_2$  binding than those of related  $[\text{Fe}^{\text{II}}_2(\text{N-Et-HPTB})(\text{OBz})](\text{BF}_4)_2$  ( $-60^\circ\text{C}$ ) and  $[\text{Fe}^{\text{II}}_2(\text{Me}_4\text{-TPDP})(\text{OBz})(\text{H}_2\text{O})](\text{BF}_4)_2$  ( $-40^\circ\text{C}$ ) complexes. Decreasing



**Figure 5.**  $^1\text{H}$  NMR spectrum of the decomposed  $1/\text{O}_2$  adduct in  $\text{CD}_3\text{CN}$ . Inset: X-band EPR spectrum of decomposed  $1/\text{O}_2$  adduct at 4 K.

the thermal stability of  $\mu\text{-peroxo}$  intermediate allows to form a metastable mixed-valence complex. In order to identify the mixed-valence intermediate and oxygenation process, we plan to perform the resonance Raman experiment with isotope labeled  $^{18}\text{O}_2$ .

**Acknowledgment.** This work was supported by Korea University and the Basic Science Research Institute Program (Project No. BSRI-95-3407).

## References

- (a) Lippard, S. J. *Angew. Chem. Intl. Ed. Engl.* **1988**, *27*, 344-361. (b) Sanders-Loehr, J. In *Iron Carriers and Iron Proteins*; Loehr, T. M., Ed.; VCH Publishers: New York, 1989; Vol. 5; 373-466. (c) Que, L., Jr.; True, A. E. *Prog. Inorg. Chem.* **1990**, *38*, 97-200. (d) Feig, A. L.; Lippard, S. J. *Chem. Rev.* **1994**, *94*, 759-805. (e) Anderson, K. K.; Oliver-Lilley, G. L.; Averill, B. A. *Advances in Inorganic Chemistry* **1995**, *43*, 359-408.
- (a) Klotz, I. M.; Kurtz, D. M., Jr. *Acc. Chem. Res.* **1984**, *17*, 16-22. (b) Wilkins, P. C.; Wilkins, R. G. *Coord. Chem. Rev.* **1987**, *79*, 195-214. (c) Stenkamp, R. E. *Chem. Rev.* **1994**, *94*, 715-726.
- (a) Stenkamp, R. E.; Sieker, L. C.; Jensen, L. H.; McCallum, J. D.; Sanders-Loehr, J. *Proc. Natl. Acad. Sci. USA* **1985**, *82*, 713-716. (b) Sheriff, S.; Hendrickson, W. A.; Smith, J. L. *J. Mol. Biol.* **1987**, *197*, 273-296. (c) Holmes, M. A.; Trong, I. L.; Turley, S.; Sieker, L. C.; Stenkamp, R. E. *J. Mol. Biol.* **1991**, *218*, 583-593.
- (a) Reichard, P.; Ehrenberg, A. *Science* (Washington, D. C.) **1983**, *221*, 514-519. (b) Lynch, J. B.; Juarez-Garcia, C.; Münck, E.; Que, L., Jr. *J. Biol. Chem.* **1989**, *264*, 8091-8096. (c) Sahlin, M.; Gräslund, A.; Petersson, L.; Ehrenberg, A.; Sjöberg, B.-M. *Biochemistry* **1989**, *28*, 2618-2625. (d) Nordlund, P.; Sjöberg, B.-M.; Eklund, H. *Nature* **1990**, *345*, 593-598.
- (a) Bollinger, J. M.; Edmonson, D. E.; Huynh, B. H.; Filley, J., Jr.; Norton, N. R.; Stubbe, J. *Science* **1991**, *253*, 292-298. (b) Ravi, N.; Bollinger, J. M.; Huynh, B. H.

- Edmonson, D. E.; Stubbe, J. J. *Am. Chem. Soc.* **1994**, *116*, 8007-8014. (c) Bollinger, J. M.; Tong, W. H.; Ravi, N.; Huynh, B. H.; Edmonson, D. E.; Stubbe, J. J. *Am. Chem. Soc.* **1994**, *116*, 8015-8023. (d) Bollinger, J. M.; Tong, W. H.; Ravi, N.; Huynh, B. H.; Edmonson, D. E.; Stubbe, J. J. *Am. Chem. Soc.* **1994**, *116*, 8024-8032.
6. (a) DeWitt, J. G.; Bensten, J. G.; Rosenzweig, A. C.; Hedman, B.; Green, J.; Pilkington, S.; Papaefthymiou, G. C.; Dalton, H.; Hodgson, K. O.; Lippard, S. J. *J. Am. Chem. Soc.* **1991**, *113*, 9219-9235. (b) Rosenzweig, A. C.; Frederic, C. A.; Lippard, S. J.; Nordlund, P. *Nature* **1993**, *366*, 537-543. (c) Rosenzweig, A. C.; Nordlund, P.; Takahara, P. M.; Frederic, C. A.; Lippard, S. J. *Chem. Biol.* **1995**, *2*, 409-418. (d) Liu, K. E.; Valentine, A. M.; Wang, D.; Huynh, B. H.; Edmonson, D. E.; Salifoglou, A.; Lippard, S. J. *J. Am. Chem. Soc.* **1995**, *117*, 10174-10185. (e) Liu, K. E.; Lippard, S. J. *Advances in Inorganic Chemistry* **1995**, *42*, 263-289.
7. (a) Fox, B. G.; Surerus, K. K.; Münck, E.; Lipscomb, J. D. *J. Biol. Chem.* **1988**, *263*, 10553-10556. (b) Fox, B. G.; Froland, W. A.; Dege, J. E.; Lipscomb, J. D. *J. Biol. Chem.* **1989**, *264*, 10023-10033.
8. Shiemke, A. K.; Loehr, T. M.; Sanders-Loehr, J. J. *Am. Chem. Soc.* **1984**, *106*, 4951-4956.
9. Kurtz, D. M. Jr. *Chem. Rev.* **1990**, *90*, 585-606.
10. (a) Chaudhuri, P.; Wieghardt, K.; Nuber, B.; Weiss, J. *Angew. Chem. Intl. Ed. Engl.* **1985**, *24*, 778-779. (b) Hartman, J. R.; Rardin, R. L.; Chaudhuri, P.; Pohl, K.; Wieghardt, K.; Nuber, B.; Weiss, J.; Papaefthymiou, G. C.; Frankel, R. B.; Lippard, S. J. *J. Am. Chem. Soc.* **1987**, *109*, 7387-7396.
11. (a) Tolman, W. B.; Bino, A.; Lippard, S. J. *J. Am. Chem. Soc.* **1989**, *111*, 8522-8523. (b) Tolman, W. B.; Liu, S.; Bentsen, J. G.; Lippard, S. J. *J. Am. Chem. Soc.* **1991**, *113*, 152-164.
12. (a) Suzuki, M.; Kanatomi, H.; Murase, I. *Chem. Lett.* **1981**, 1745-1748. (b) Suzuki, M.; Uehara, A.; Oshio, H.; Endo, K.; Yanaga, M.; Kida, S.; Satito, K. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 3547-3555.
13. (a) Borovik, A. S.; Que, L., Jr. *J. Am. Chem. Soc.* **1988**, *110*, 2345-2346. (b) Borovik, A. S.; Hendrich, M. P.; Holman, T. R.; Münck, E.; Papaefthymiou, G. C.; Que, L., Jr. *J. Am. Chem. Soc.* **1990**, *112*, 6031-6038.
14. (a) Nishida, Y.; Takeuchi, M.; Shimo, H.; Kida, S. *Inorg. Chim. Acta* **1984**, *96*, 115-119. (b) Murch, B. P.; Bradley, F. C.; Que, L., Jr. *J. Am. Chem. Soc.* **1986**, *108*, 5027-5028. (c) Micklitz, W.; Bott, S. G.; Bentsen, J. G.; Lippard, S. J. *J. Am. Chem. Soc.* **1989**, *111*, 372-374. (d) Leising, R. A.; Brennan, B. A.; Que, L., Jr.; Fox, B. G.; Münck, E. *J. Am. Chem. Soc.* **1991**, *113*, 3988-3990. (e) Dong, Y.; Fujii, H.; Hendrich, M. P.; Leising, R. A.; Pan, G.; Randall, C. R.; Wilkinson, E. C.; Zang, Y.; Que, L., Jr.; Fox, B. G.; Kauffmann, K.; Münck, E. *J. Am. Chem. Soc.* **1995**, *117*, 2778-2792.
15. Kitajima, N.; Tamura, N.; Tanaka, M.; Moro-oka, Y. *Inorg. Chem.* **1992**, *31*, 3342-3343.
16. Abbreviations used: HB(3,5-i-Pr<sub>2</sub>pz)<sub>3</sub>, hydrotris(3,5-diisopropyl-1-pyrazolyl)borate; OBz, benzoate; N-Et-HPTB, N, N, N', N'-tetrakis(N-ethyl-2-benzimidazolylmethyl)-1,3-diaminopropan-2-olate; HPTP, N, N, N', N'-tetrakis(2-pyridylmethyl)-1,3-diaminopropan-2-olate; Me<sub>4</sub>-TPDP, N, N, N', N'-tetrakis[6-methyl-2-pyridyl)methyl]-1,3-diaminopropan-2-olate.
17. (a) Ménage, S.; Brennan, B. A.; Juarez-Garcia, C.; Münck, E.; Que, L., Jr. *J. Am. Chem. Soc.* **1990**, *112*, 6423-6425. (b) Dong, Y.; Ménage, S.; Brennan, B. A.; Elgren, T. E.; Jang, H. G.; Pearce, L. L.; Que, L. *J. Am. Chem. Soc.* **1993**, *115*, 1851-1859.
18. (a) Hayashi, Y.; Suzuki, M.; Uehara, A.; Mizutani, Y.; Kitagawa, T. *Chem. Lett.* **1992**, 91-94. (b) Hayashi, Y.; Kayatani, T.; Sugimoto, H.; Suzuki, M.; Inomata, K.; Uehara, A.; Kitagawa, T.; Maeda, Y. *J. Am. Chem. Soc.* **1995**, *117*, 11220-11229.
19. McKee, V.; Zvagulis, M.; Dagdigian, J. V.; Patch, M. G.; Reed, C. A. *J. Am. Chem. Soc.* **1984**, *106*, 4765-4772.
20. Hendrich, M. P.; Pearce, L. L.; Que, L., Jr.; Chasteen, N. D.; Day, E. P. *J. Am. Chem. Soc.* **1991**, *113*, 3039-3044.
21. Hendrich, M. P.; Münck, E.; Fox, B. G.; Lipscomb, J. D. *J. Am. Chem. Soc.* **1990**, *112*, 5861-5865.
22. Bertini, I.; Luchinat, C. in *NMR of Paramagnetic Molecules in Biological Systems*; The Benjamin/Cummings Publishing Company Inc.: CA, U. S. A., 1986; Chapter 7.
23. Ming, L.; Jang, H. G.; Que, L., Jr. *Inorg. Chem.* **1992**, *31*, 359-364.
24. Münck, E.; Debrunner, P. G.; Tsibris, J. M.; Gunsalus, I. C. *Biochemistry* **1972**, *11*, 855.
25. (a) Feig, A. L.; Lippard, S. J. *J. Am. Chem. Soc.* **1994**, *116*, 8410-8411. (b) Feig, A. L.; Becker, M.; Schindler, S.; Eldik, R.; Lippard, S. J. *Inorg. Chem.* **1996**, *35*, 2590-2601.
26. Chen, Q.; Lynch, J. B.; Gomez-Romero, P.; Ben-Hussein, A.; Jameson, G. B.; O'Connor, C. J.; Que, L., Jr. *Inorg. Chem.* **1988**, *27*, 2673-2681.